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# Time Resolved Broadband Terahertz Relaxation Dynamics of Electron in Water

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**Abstract**—we investigated the transient response of the solvated electron ejected by photodetachment from potassium ferrocyanide in water using time resolved terahertz spectroscopy (TSTS). We find that the measured frequency dependent conductivity can be well described by a Drude-Smith model, supplemented by a Lorentz model oscillating near 5 THz.

## I. INTRODUCTION

THE electron solvation response in water has been a topic of intense experimental and theoretical investigations for many years[1–3]. It is well known that after an electron is injected into water by directly ionization of water molecule or photodetachment of anions through charge transfer to solvent (CTTS), the quasi-free electron will become trapped and relax to a fully solvated state. However, the detailed picture of electron relaxation process still needs further investigation.

In this paper we will investigate the electron relaxation process by directly measuring the optical conductivity using time resolved terahertz spectroscopy (TRTS)[4, 5]. TRTS is not only useful for characterizing charge carriers under steady state conditions, but is also qualified for nonequilibrium measurements. In the experiment we use air photonics terahertz time domain spectroscopy (THz-TDS) setup [6], which gives usable bandwidth up to 12 THz. The electron in water is injected by photodetachment from  $K_4Fe(CN)_6$  using UV pump at 267 nm. The anion  $[Fe(CN)_6]^{4-}$  has a high quantum yield with one photon absorption at 267 nm. The 267 nm UV pulse with pulse energy of 30  $\mu J$  is generated by frequency tripling part of the fundamental 800 nm pulse. The water sample is prepared by using a gravity driven free flowing liquid film with thickness of 30  $\mu m$ . To avoid the anion oxidation and water vapor absorption line in the terahertz region, the whole set up is placed in a continuously nitrogen purged box. Ultrabroadband THz transients are generated and detected by a two-color femtosecond-induced air plasma and air biased coherent detection, respectively. To be able to measure the weak signal induced by the pump, an avalanche photodiode (APD) together with a boxcar averager is used in the detection. Time traces of the differential and reference signals were measured simultaneously.

## II. RESULTS

Figure 1 shows the pump induced differential THz waveform transmitting through the water film. The whole relaxation process happens in a few hundred fs, followed by a nonzero component lasting more than 10 ps. This is likely due to the slow recombination rate of electron with their donor anion.

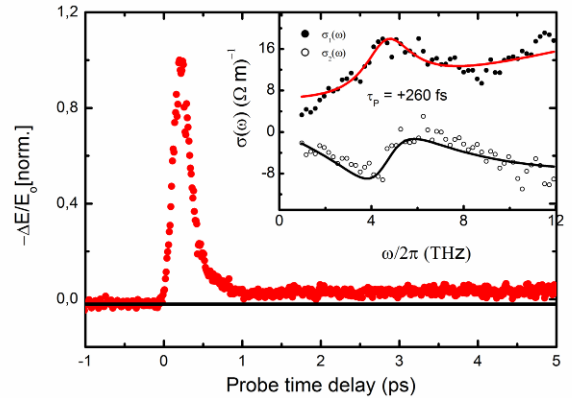
The frequency-dependent optical conductivity of electrons

in water 260 fs after excitation is plotted in the inset of Fig. 1. Our measured conductivity data can be well described with a Drude-Smith model plus a Lorentz model oscillating near 5 THz. The conductivity is given by

$$\tilde{\sigma}(\omega) = \frac{\omega_p^2 \epsilon_0 \tau_1}{1 - i\omega\tau_1} \left(1 + \frac{c}{1 - i\omega\tau_1}\right) + \frac{\omega_p^2 \epsilon_0 \omega}{\omega/\tau_2 + i(\omega_0^2 - \omega^2)} \quad (1)$$

Where  $\omega_p$  is the plasma frequency,  $\omega_0$  is the resonance frequency,  $\tau$  is the carrier scattering time and  $c$  is a constant describing the degree of electron confinement.

In summary, we have shown the frequency resolved optical conductivity of electrons in water 260 fs after excitation, which is well fitted with Drude-Smith model plus a Lorentz model resonating near 5 THz.



**Fig. 1.** Negative differential THz transmission of water film as a function of pump-probe delay time. The inset shows the complex conductivity of water at  $\tau_p = +260$  fs (the black solid dot data is the real part of the conductivity and the circle dot data is the imaginary part of the conductivity; the red line and black line are corresponding fitting to Drude-Smith model plus Lorentz model with fitting parameters:  $\omega_p/2\pi = 7.8$  THz,  $\omega_p/2\pi = 0.93$  THz,  $\omega_0/2\pi = 4.7$  THz,  $\tau_1 = 4.77$  fs,  $\tau_2 = 64$  fs,  $c = -0.8717$ ).

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